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Mineral paragenesis in a talc–water experimental hydrothermal system

GENE WHITNEY AND DENNIS D. EBERL

U.S. Geological Survey
Denver, Colorado 80225

Abstract

Gel having a Mg:Si ratio identical to that of talc (3:4) was treated hydrothermally at six temperatures between 300° C and 550° C and 1 kbar for times of 7, 30, 50, 120 and 200 days in order to identify reaction trends. Talc crystallized first at all temperatures. It then reacted to form stevensite at temperatures between 300° C and 450° C. At 400° C and 450° C, stevensite continued to react to form a perfectly ordered mixed-layer stevensite/chlorite (corrensite-like structure). At 500° C and 550° C the initially formed talc improved in crystallinity with time and showed no further reactions. Natural talc starting material showed trends similar to that of the gels, reacting to form stevensite at 350° C in a 30-day run. The reaction trends suggest that stevensite and/or the corrensite-like phase are the stable minerals at 450° C and below in systems with chemistry similar to that of these experiments.

Introduction

Talc frequently occurs in magnesium-rich metamorphic rocks and in hydrothermally altered ultramafic rocks. Previous hydrothermal experiments have supported the observations made on rocks that talc is stable at high temperatures, but that its stability at low temperatures is uncertain. Although it is not abundant in sediments, authigenic talc has been identified in evaporites (Dreizler, 1962; Langbein, 1961; Raymond, 1962; Stewart, 1949) and in unmetamorphosed carbonates (Millot and Palausi, 1959).

In previous hydrothermal experiments, talc has been synthesized at temperatures above 490° C by Bowen and Tuttle (1949), Greenwood (1963), Kitahara *et al.* (1966), Pistorius (1963), Schreyer and Seifert (1969), and Yoder (1952). Johannes (1969) attempted to determine the low-temperature stability limit of talc in a CO_2-bearing system but was unable to produce talc below 320° C after 320 days. Bricker *et al.* (1973) sought to determine whether talc is stable at low temperatures using dissolution experiments. They derived the Gibbs free energy of talc at 25° C, but their calculations were disputed by Hemley *et al.* (1977a). Hemley *et al.* (1977a, 1977b) studied the solubility of talc at elevated pressures and suggested that "Mg-montmorillonite" (stevensite?) may be the low-temperature stable equivalent of talc, although they do not report finding such a mineral in their run products.

Stevensite ($Mg_{3-x}Si_4O_{10}(OH)_2{\cdot}nH_2O$) is a member of the smectite group of clay minerals. It has a chemical composition similar to that of talc ($Mg_3Si_4O_{10}(OH)_2$), differing from talc primarily in water content (Brindley *et al.*, 1977). Like other smectites, stevensite has a negative layer charge and expands in the presence of ethylene glycol. Unlike other smectites, however, stevensite derives its layer charge from octahedral vacancies rather than from isomorphous substitutions.

Stevensite has been synthesized at low temperatures by Caillere *et al.* (1963), Roy and Roy (1955), Strese and Hofmann (1941), and Bowen and Tuttle (1949). The stevensite from the latter work was identified by Faust *et al.* (1959). In each study, stevensite was synthesized at relatively low temperatures, and its synthesis was incidental to the objectives of the investigations. No systematic study of stevensite synthesis has been pursued, and its genetic relationship to talc is not understood.

Natural stevensite is uncommon, but has been identified as an alteration product of basalt (Leeds, 1873; Brindley, 1955; Brindley *et al.*, 1977; Faust *et al.*, 1953, 1959) and in desert playa deposits (Bradley and Fahey, 1962; Tettenhorst and Moore, 1978; Khoury, 1978). Stevensite occurring with talc has been reported by DeRudder and Beck (1963) and Imai *et al.* (1970), who describe both minerals in hydrothermal veins cutting wollastonite-rich rocks. The progressive magnesium metasomatism of wollastonite produced a zoned vein in which talc occu-

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pied the most intensely altered central portion, whereas stevensite was found in the peripheral portion.

In addition to stevensite and talc, a perfectly ordered mixed-layer stevensite/chlorite was produced in our experiments. It is similar in structure to the mineral corrensite, which has been variously defined as a trioctahedral, perfectly ordered mixed-layer chlorite/swelling chlorite, chlorite/smectite and chlorite/vermiculite (Bailey, 1975). The chlorite/smectite phase was synthesized in aluminum-bearing systems between 445° C and 465° C by Velde (1973), and between 400° C and 600° C by Wyart and Sabatier (1966). Natural corrensites are common in magnesium-rich saline or hypersaline environments (Bodine, 1978; Earley *et al.*, 1956; Earley and Milne, 1956; Fournier, 1961; Grim *et al.*, 1960; Kopp and Fallis, 1974; Kubler, 1973; Lippmann, 1956), or in hydrothermal veins (Blatter *et al.*, 1973; April, 1980).

Experimental methods

The starting material was either amorphous gel, prepared by the method of Hamilton and Henderson (1968), or powdered natural talc from Fowler, New York (Ward's Natural Science Establishment). The gel had a Mg:Si ratio of 3:4, identical to that of talc. Each run was prepared by introducing 30 mg of the gel or talc into a gold tube (2.54 mm I.D., 3.05 mm O.D.) containing 30 μl of triply distilled, deionized water. The capsule was welded shut and weighed before and after treatment. The samples were placed in calibrated rod-type reaction vessels and heated in resistance furnaces. Temperatures were maintained within ±5° C of the reported temperature by on-off controllers.

Gels were treated at 300° C, 350° C, 400° C, 450° C, 500° C and 550° C for 7, 30, 50, 120 and 200 days. The natural talc was treated at the above temperatures, but for run times of 7 and 30 days only. The pressure was held constant at 1 kbar for all runs.

The solid run products were gently disaggregated in a mortar and pestle, and pipetted onto glass slides. The oriented samples were examined by X-ray diffraction using Ni-filtered copper K_α radiation. Samples were X-rayed after air-drying, after exposure to ethylene glycol, and after various heat treatments. X-ray diffraction patterns of some of the mixed-layer minerals were calculated using a modified version of the computer program of Reynolds and Hower (1970).

Results

After 7 days the gel had crystallized to talc at all temperatures. This talc then continued to react as run times increased. In the 300° C and 350° C runs, the talc degraded with increasing time, as shown by the diminution and broadening of its X-ray peaks, while stevensite appeared and increased in abundance (Fig. 1). The width at half-height of the diffraction peak near 9.4Å was used to calculate the thickness (imperfection free distance) of the talc crystallites by using the Scherrer equation (Klug and Alexander, 1974, p. 687). The results of this calculation (Fig. 2) indicate that the talc crystallites undergo a dramatic decrease in size along the *c*-axis with increasing time, at least through 120 days. The apparent small increase in crystallite size between 120 and 200 days may be real. If so, it is not understood. Although change in crystallite size was not plotted for stevensite, it is apparent from Figure 1 that it increases with increasing time.

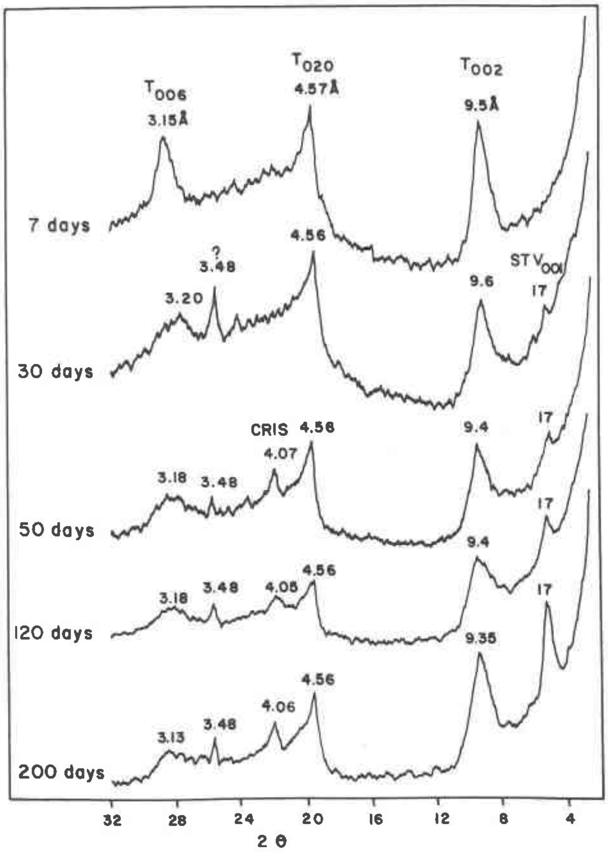

Fig. 1. X-ray diffractograms of run products formed from the gel treated hydrothermally at 350° C for the times shown. All samples are oriented and glycolated. T = talc, STV = stevensite, CRIS = cristobalite.

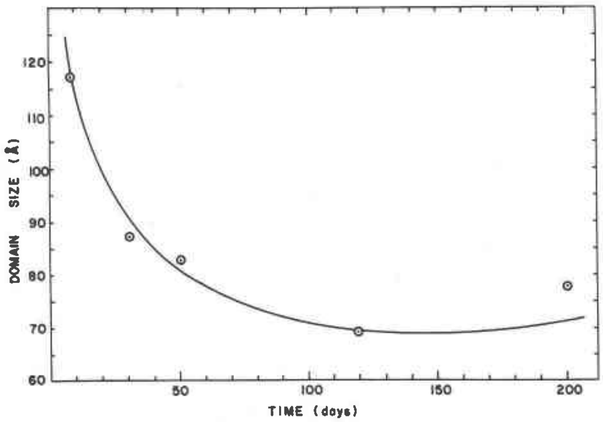

Fig. 2. The change in crystallite (domain) size of talc as a function of time at 350° C, calculated using the Scherrer equation with measurements made of the X-ray peaks in Figure 1. Crystallite dimensions are approximate and show only relative changes with time.

Because the nature of the starting material may affect the course of the reactions, parallel runs were made using natural talc as starting material. Stevensite also formed from natural talc at 350° C.

At 400° C the gel runs follow a reaction trend from talc to stevensite in the short runs, but stevensite gives way to perfectly ordered mixed-layer stevensite/chlorite in the long runs. (Fig. 3). The same reaction trend was seen at 450° C, but the reaction proceeded more rapidly. The ordered stevensite/chlorite which occurred in the 200-day run at 450° C is shown in Figure 4 after various treatments, along with a calculated diffraction pattern for a glycolated sample. At 400° C and 450° C the degradation of talc is not nearly so pronounced as at lower temperatures, but still occurs. Mixed-layer stevensite/chlorite, which forms at the expense of talc and stevensite, improves in crystallinity with time.

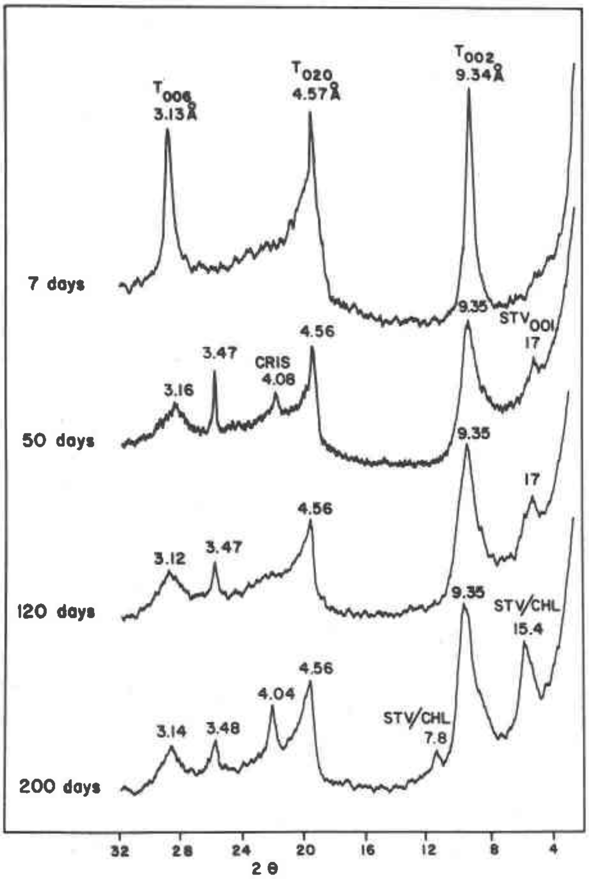

Fig. 3. X-ray diffractograms of run products formed from the gel at 400° C, showing the development of the ordered stevensite/chlorite. Samples are oriented and glycolated. T = talc, STV = stevensite. STV/CHL = mixed-layer stevensite/chlorite, CRIS = cristobalite.

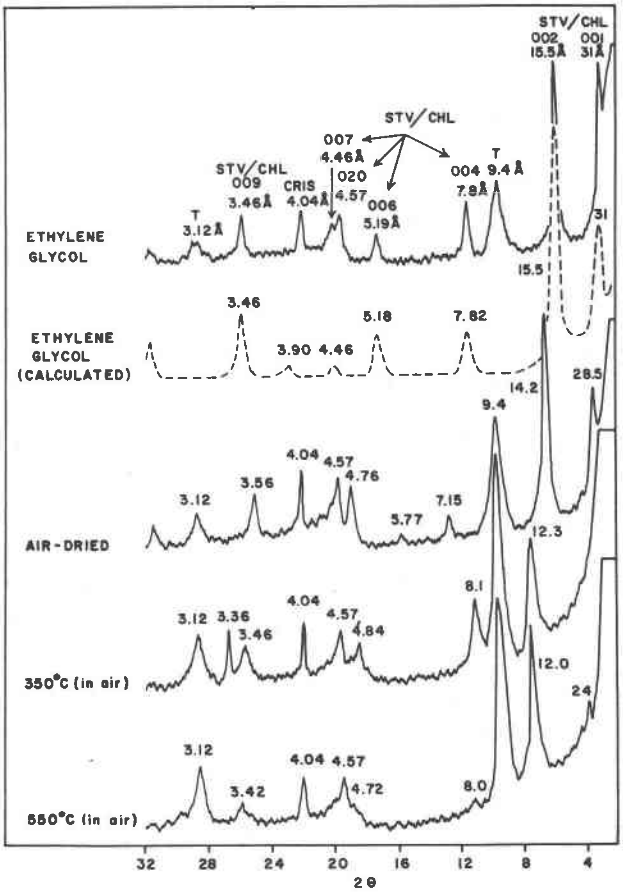

Fig. 4. X-ray diffractograms of the perfectly ordered mixed-layer stevensite/chlorite which formed from gel after 200 days at 450° C. The different X-ray patterns represent the same sample after the treatments indicated. STV/CHL = mixed-layer stevensite/chlorite, T = talc, CRIS = cristobalite.

At 500° C and 550° C talc crystallized initially and persisted through the longest runs, improving slightly in crystallinity with time.

Additional phases which occur in several runs at temperatures of 450° C or lower are cristobalite, and an unidentified mineral which gives a single sharp X-ray peak at 3.48Å.

Discussion

The rapid growth of talc from the gel starting material is not unusual. Talc is easy to crystallize. For example, Greenwood (1963) observed that oxide mixtures of talc composition had become 50 percent talc after only half an hour at 650° C, and Yoder (1952) found that talc not only crystallized rapidly over a wide range of temperatures, but that it frequently crystallized outside its stability field and then reacted toward stable phases.

The disappearance of talc with increasing time indicates that it is not stable at 300° C or 350° C in these experiments. The growth of stevensite suggests that stevensite may be the preferred phase at low temperatures in this closed system.

As mentioned above, the perfectly ordered mixed-layer stevensite/chlorite synthesized at 400° C and 450° C is similar to corrensite. The chemistry of the experimental system suggests that the layer charge required for expansion of the smectite layers is derived from octahedral vacancies because no other charge-building mechanisms are available. The 2:1 layer of the chlorite must be held to the interlayer hydroxide sheet by hydrogen bonding alone, as electrostatic bonding would require a net positive charge on the hydroxide sheet, and no known mechanism for building such a charge exists in this chemically simple system. Bish and Giese (1981) have shown, using calculated interlayer bonding energies, that hydrogen bonding is sufficient to hold chlorite (Ib) layers together even in the absence of electrostatic bonding.

The time-lapse nature of these experiments permits an examination of reaction mechanisms. The reaction of talc to stevensite could theoretically proceed via layer transformation or via dissolution and reprecipitation. During transformation, talc layers would be converted gradually into stevensite layers by the movement of some octahedral magnesium into the interlayer position according to the following idealized reaction:

$$(Mg_3)^{VI}Si_4O_{10}(OH)_2 + nH_2O \rightarrow (Mg_{2.7}\square_{0.3})^{VI}Si_4O_{10}(OH)_2[(Mg^{2+}_{0.3})\cdot nH_2O]$$

where □ indicates a vacancy. If this type of layer transformation proceeded randomly within a crystallite, the result would be a random mixed-layer talc/stevensite. Calculations of mixed-layer talc/stevensite diffractograms using the computer program of Reynolds and Hower (1970) reveal that the formation of a mixed-layer intermediate phase would cause a migration of the 9.4Å talc peak towards 8.5Å as the proportion of stevensite layers increased. No such migration is observed in these experiments, suggesting that a mixed-layer intermediate phase was not formed.

The diminution and broadening of the talc X-ray diffraction peaks and the simultaneous growth and sharpening of the stevensite peaks suggest, rather, that the talc dissolves while stevensite nucleates and grows at its expense. A third possibility is that the talc is converted to stevensite, layer by layer, but that the stevensite layers form in contiguous zones within crystallites rather than forming as isolated layers scattered throughout the talc crystallites. This mechanism would produce the appearance of the simultaneous growth of stevensite and the diminution of talc since the X-ray diffractometer would "see" the zones as separate phases. Either of the two latter mechanisms would produce the observed data.

Kerolite may form in some of the runs as an intermediate stage in the reaction of talc to stevensite. Brindley *et al.* (1977) defined kerolite as a highly disordered variety of talc that exhibits slightly enlarged basal spacing which results from the misfit of basal oxygens of adjacent layers. The slightly enlarged basal spacing for some of the talc (Fig. 1) suggests that kerolite may be forming, but no systematic relationship is evident.

The conversion of stevensite to the perfectly ordered mixed-layer stevensite/chlorite in the longest runs at 400° C and 450° C requires that hydroxide sheets be precipitated between alternate layers of stevensite, thereby converting half of the layers to chlorite. This reaction requires that stevensite possess a propensity for ordering, and requires a change in solution chemistry to account for the precipitation of hydroxide sheets. The change in chemistry of the solutions must be monitored in order to understand this problem more fully.

Because the reaction of stevensite layers to chlorite layers requires an increase in the interlayer magnesium population, some of the stevensite or talc layers must break down to provide the extra magnesium. Such a reaction would release silica, thereby explaining the formation of cristobalite as a reaction product.

The experiments suggest that natural analogs may exhibit the sequence talc → kerolite(?) → stevensite → corrensite with increasing temperature and reaction time. One place where such a pattern might be found is in the ocean basins. Talc and trioctahedral smectite have been identified as alteration products of oceanic basalts (Seiver and Kastner, 1967; Bass, 1976), and it is possible that some of the magnesium smectites in these rocks are stevensite, as very careful chemical analyses must be used to distinguish stevensite from saponite.

Summary

The talc–water system is chemically simple, yet reveals a surprisingly varied mineralogy in hydrothermal experiments. At 450° C and below, the paragenetic sequence is: gel → talc → kerolite(?) → stevensite → mixed layer stevensite/chlorite with increasing run time and temperature. At 500° C and above, only talc crystallizes and persists.

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